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(54) Aromatic polysulfone resin composition.

(57) An aromatic polysulfone resin composition comprises 20 to 80% by weight of an aromatic polysulfone, 10 to 70% by weight of a fibrous reinforcement or an inorganic filler, and 0.5 to 20% by weight of a fluororesin. The aromatic polysulfone resin composition has heat resistance, strength, stiffness, flame resistance and processability superior to known sulfone resins and is particularly useful as an engineering plastics material.

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AROMATIC POLYSULFONE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to an aromatic polysulfone resin composition exhibiting high heat resistance, superior mechanical properties, low mold shrinkage, and good mold releasability.

DESCRIPTION OF THE PRIOR ART

Aromatic polysulfone resins are noticed as engineering plastics superior in heat resistance, strength, stiffness, flame resistance, chemical resistance, processability, etc., particularly in the fields of applications to electric parts and automotive parts.

In these application fields, however, there is a growing need, with technical progress in these fields, for an aromatic polysulfone resin composition having higher heat resistance, stiffness, and dimensional accuracy (low mold shrinkage) while maintaining the flame resistance, chemical resistance, hot water resistance, and processability which are merits of this resin.

It is known that the heat resistance, stiffness, and dimensional accuracy of resins are improved, as a rule, by incorporating thereinto a fibrous reinforcement such as glass fiber, carbon fiber, or the like or an inorganic filler in powdery, acicular, or flaky form, such as talc, calcium carbonate, magnesium carbonate,

calcium sulfite, aluminum hydroxide, mica, molybdenum disulfide, wollastonite, graphite, titanium white, or glass beads.

Also when aromatic polysulfone resin is compounded with such a reinforcement or filler, improvements in the heat resistance and stiffness and a decrease in the mold shrinkage are observed responsively to the quantity of the reinforcement or filler blended.

With the increase of quantity of the reinforcement or filler blended, the mold shrinkage decreases and the mold fidelity in injection molding and in similar molding becomes better; but the mold releasability in injection molding lowers and the take-off of the molded article from the mold cavity becomes difficult. In consequence, excess stress is exerted on the molded article when it is ejected from the cavity; this leaves strain in the molded article and may cause troubles such as the deformation of the molded article at the time of the ejection and the stress cracking and eventual break of the finished article.

Accordingly, in spite of the strong request for a resin composition exhibiting low mold shrinkage and excellent mold fidelity and dimensional accuracy, the quantity of the reinforcement or filler to be blended is usually restricted so as to hold the reduction of the mold shrinkage in such a degree that none of the above problems arise in the operation of releasing the molded article from the mold cavity.

In view of the above, the present inventors made intensive studies, and as a result, found that a resin composition which has high heat resistance, stiffness, and strength and exhibits low mold shrinkage and good mold releasability can be obtained by compounding an aromatic polysulfone with a fibrous reinforcement or an inorganic filler and additionally with a specified amount of a fluororesin. Based on this finding, this invention has been accomplished.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an aromatic polysulfone resin composition excellent in processability as well as in heat resistance, stiffness, and strength.

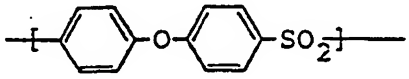
Other objects and advantages of the present invention will be apparent from the following description.

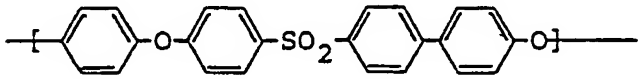
According to the present invention, there is provided an aromatic polysulfone resin composition which comprises 20 to 80% by weight of an aromatic polysulfone, 10 to 70% by weight of a fibrous reinforcement or an inorganic filler, and 0.5 to 20% by weight of a fluororesin.

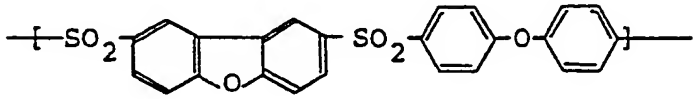
DETAILED DESCRIPTION OF THE INVENTION

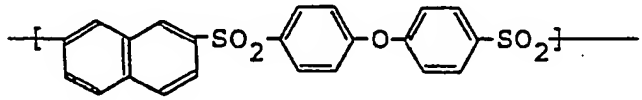
The aromatic polysulfone to be used as a component of the composition of this invention may be a polyarylene compound in which arylene units together

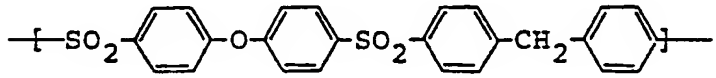
with ether linkages and with sulfone linkages are arranged orderly or disorderly. Polymers of the following structures (1) - (16) are given as examples of the aromatic polysulfone. Of these polymers, particularly preferred are those of the structures (1), (2), and (6) in that physical properties and processability thereof are well balanced.

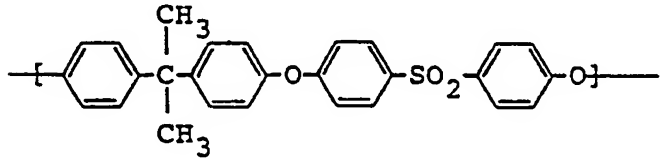
(1) 

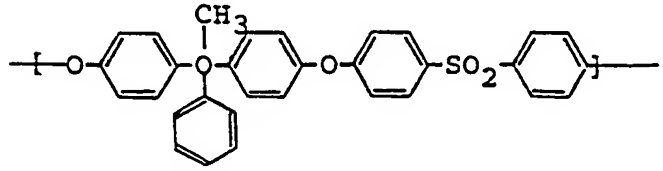
(2) 

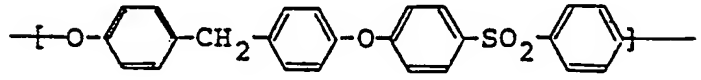
(3) 

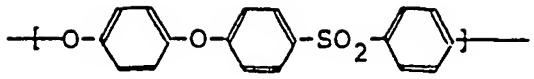
(4) 

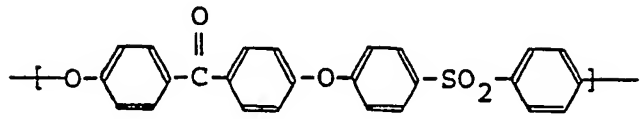
(5) 

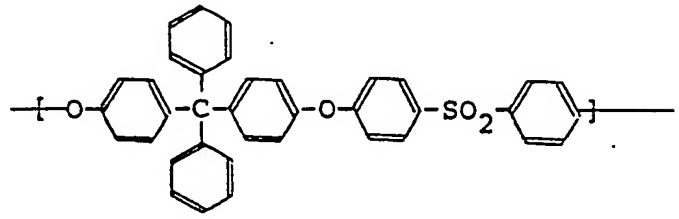
(6) 

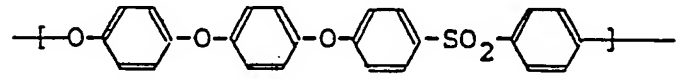
(7) 

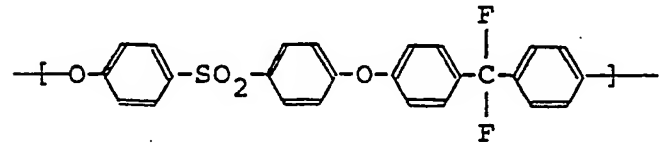
(8) 

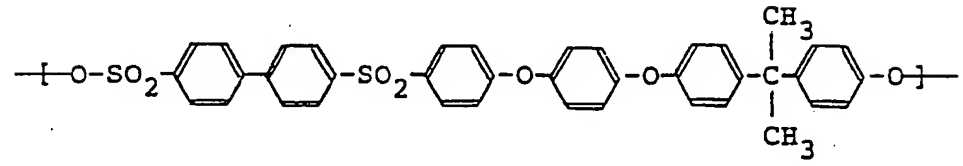
(9) 

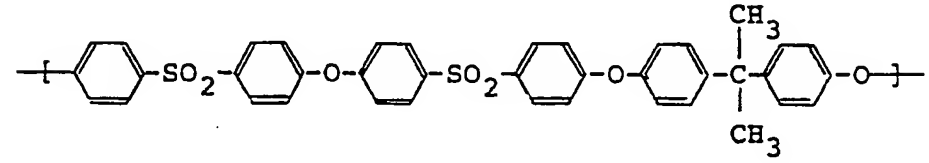
(10) 

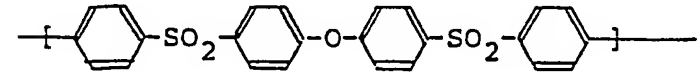
(11) 

(12) 

(13) 

(14) 

(15) 

(16) 

Further, the aromatic polysulfones exhibiting a reduced viscosity of 0.3 - 0.6, as determined at 25°C on a 1 W/V % solution of the polymer in dimethylformamide, are best suited because these are excellent in the balance of physical properties such as heat resistance, stiffness, and strength with processability.

Examples of the fibrous reinforcement used as another component of the composition of this invention are glass fiber, carbon fiber, aromatic polyamide fiber, silicon carbide fiber, silicon nitride fiber, alumina fiber, potassium titanate fiber, and mineral fibers; that is, fibrous reinforcements generally used for improving the heat resistance, strength, stiffness, etc. of resins can also be used herein.

Examples of the inorganic filler used as another component of the composition of this invention (additionally or alternatively to the fibrous reinforcement) are talc, calcium carbonate, magnesium carbonate, calcium sulfite, aluminum hydroxide, mica, molybdenum disulfide, wollastonite, graphite, titanium white, glass beads, zirconia, and silica.

These fibrous reinforcements and inorganic fillers can be used normally as such without any treatment, but also used after treatment thereof with a silane coupling agent such as an aminosilane or an epoxysilane or with chromic chloride for the purpose of enhancing the affinity for the aromatic polysulfone, or with other surface treating agents which meet individual purposes.

The fluororesin used as another component of

the composition of this invention is a macromolecular compound containing fluorine atoms in the molecule. Examples thereof are tetrafluoroethylene resin, tetrafluoroethylene-perchloroalkyl vinyl ether copolymer resin, tetrafluoroethylene-hexafluoropropylene copolymer resin, tetrafluoroethylene-ethylene copolymer resin, chlorotrifluoroethylene resin, and vinylidene fluoride resin.

Of these fluororesins, tetrafluoroethylene resin (polytetrafluoroethylene) is preferable for the following reason: This polymer has a high melt viscosity and hence hardly flows even when heated to temperatures above its melting point (about 330°C). Therefore its state of dispersion in the aromatic polysulfone is little altered under the usual conditions of molding the resin composition, so that characteristics, mechanical strengths, and mold releasability in injection molding, of the composition are scarcely varied by molding.

Suitable blending proportions of these components of the composition are 20 to 80% by weight of the aromatic polysulfone, 10 to 70% by weight of the fibrous reinforcement or inorganic filler, and 0.5 to 20% by weight of the fluororesin, based on the total weight of the composition, wherein the combined proportion of the fibrous reinforcement or inorganic filler with the fluororesin is desired to be in the range of 20 to 80% by weight.

When the combined proportion of the reinforcement or filler with fluororesin is more than 80% by weight and the proportion of the aromatic polysulfone is

less than 20% by weight, sufficient mixing of the components is unattainable and the resulting composition is hence nonuniform, loses fluidity, and is difficult to mold. When the combined proportion of the reinforcement or filler with the fluororesin is less than 20% by weight, the sufficient effect of lowering mold shrinkage cannot be obtained.

When the proportion of the reinforcement or filler is less than 10% by weight, the effect of lowering mold shrinkage is insufficient even if the combined proportion of the reinforcement or filler with the fluororesin is 20 to 80% by weight. On the other hand, when the proportion of the fluororesin is less than 0.5% by weight, the mold releasability in injection molding is insufficient.

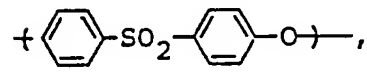
When the proportion of the reinforcement or filler exceeds 70% by weight, the compounding becomes difficult and insufficient, giving a nonuniform composition. When the proportion of the fluororesin exceeds 20% by weight, the strength of the resulting composition remarkably lowers.

The blending method for the composition of this invention is not particularly restricted. The aromatic polysulfone, the fibrous reinforcement or inorganic filler, and the fluororesin can be fed separately into a melt mixer or may be mixed in a mortar, Henschel mixer, ball mill, ribbon blender, or the like prior to the feeding into a melt mixer.

One or more usual additives can be incorporated into the composition of this invention unless departing from the object of the invention. Such additives include antioxidants, heat stabilizers, ultraviolet absorbers, lubricants, mold releasing agents, colorants such as dyes and pigments, flame retardants, auxiliary flame retardants, antistatics, etc.

The invention is illustrated in more detail with reference to the following examples; however, these examples are intended not to restrict the invention but to give preferred embodiments thereof.

Examples 1 to 5

A polyethersulfone having the basic structure  , (the reduced viscosity was 0.4, as determined at 25°C on a 1 W/V % solution of the polymer in dimethylformamide), wollastonite ($CaSiO_3$ in acicular form, supplied by Nagase & Company, Ltd. under the tradename of NYAD-G), and tetrafluoroethylene resin (supplied by Imperial Chemical Industries Ltd. under the tradename of Fluon L 169) were mixed in proportions as shown in Table 1. The mixture was melted and mixed at 340°C by using a twin-screw extruder (PCM-30, supplied by Ikegai Corporation). The resulting strands were cold and cut into pellets.

Pellets thus obtained were injection-molded (Sumitomo-Nestal 47/28 injection molding machine, cylinder

temperature 360°C, mold temperature 130°C) into bending test specimens. After the mold was opened, the resistance against the ejection of each molded part with the ejector pin was measured by using a strain gage type of pressure sensor.

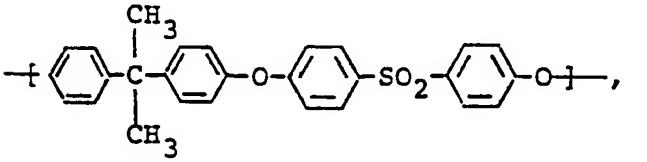
These bending test specimens were measured for flexural strength, flexural modulus, heat deflection temperature, and mold shrinkage. The flexural strength and the heat deflection temperature were determined in accordance with ASTM D-790 and ASTM D-648 (18.6 Kg/cm²), respectively. The results were summarized in Table 1.

Comparative Examples 1 to 5

The same polyethersulfone, wollastonite, and tetrafluoroethylene resin as used in Examples 1 to 5 were mixed in proportions as shown in Table 1, and molded and tested for physical properties in the same manner as in Examples 1 to 5. The results are summarized in Table 1.

Examples 6 to 10

A polysulfone having the basic structure



, (the reduced viscosity was 0.38, as determined at 25°C on a 1 W/V % solution of the polymer in dimethylformamide), glass fiber (REV-8, supplied by Nihon Sheet Glass Co., Ltd.), and tetrafluoroethylene resin (supplied by Daikin Industries, Ltd.

under the tradename of Lubron L-5) were mixed in proportions as shown in Table 2. The mixture was melted and mixed at 320°C by using a twin-screw extruder (PCM-30, supplied by Ikegai Corporation). The resulting strands were cooled with water and cut into pellets.

Pellets thus obtained were injection-molded (Sumitomo-Nestal 47/28 injection molding machine, cylinder temperature 340°C, mold temperature 110°C) into bending test specimens. The resistance against the ejection, flexural strength, flexural modulus, heat deflection temperature, and mold shrinkage were measured in the same manner as in Examples 1 to 5. The results are summarized in Table 2.

Comparative Examples 6 to 10

The same polysulfone, glass fiber and tetrafluoroethylene resin as used in Examples 6 to 10 were mixed in proportions as shown in Table 2 and molded and tested for physical properties in the same manner as in Examples 6 to 10. The results are summarized in Table 2.

Table 1

	Composition			Resistance against ejection of injection-molded article (Kg/cm²)	Mold shrinkage (%)	Flexural strength (kg/cm²)	Flexural modulus (kg/cm²)	Heat deflection temperature (°C)
	Polyethersulfone	Wollastonite	Fluororesin					
Example 1	40	55	5	130	0.1	1100	120,000	215
" 2	50	45	5	100	0.2	1200	101,000	213
" 3	70	25	5	80	0.3	1300	85,000	210
" 4	50	49	1	105	0.2	1250	110,000	215
" 5	50	40	10	95	0.2	1150	90,000	212
Comparative Example 1	100	0	0	250	0.7	1300	26,500	203
" 2	90	5	5	65	0.6	1300	27,000	205
" 3	10	85	5	Molding was infeasible				
" 4	50	20	30	70	0.5	650	65,000	210
" 5	50	49.9	0.1	500	Measurement was infeasible on account of cracks formed in molded part			

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Table 2

	Composition			Resistance against ejection of injection-molded article (Kg/cm²)	Mold shrinkage (%)	Flexural strength (Kg/cm²)	Flexural modulus (Kg/cm²)	Heat deflection temperature (°C)
	Polysulfone	Glass fiber	Fluororesin					
Example 6	40	55	5	120	0.1	1000	135,000	185
" 7	50	45	5	95	0.2	1100	110,000	182
" 8	70	25	5	70	0.3	1200	100,000	180
" 9	50	49	1	100	0.2	1150	125,000	185
" 10	50	40	10	85	0.2	1050	105,000	183
Comparative Example 6	100	0	0	230	0.7	1100	26,500	174
" 7	90	5	5	60	0.6	1100	27,000	175
" 8	10	85	5	Molding was infeasible				
" 9	50	20	30	65	0.5	500	70,000	180
" 10	50	49.9	0.1	450	Measurement was infeasible on account of cracks formed in molded part			

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The following have been revealed from the above examples and comparative examples.

The compositions according to the present invention are improved in heat resistance and stiffness (flexural modulus) as compared with the conventional aromatic polysulfone resin compositions, and exhibit high strength and additionally low mold shrinkage and good mold releasability (Examples 1 to 10).

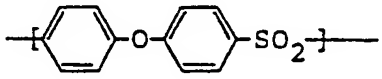
The tested compositions except those of this invention do not have the intended good properties, as those (Comparative Examples 2 and 7) have been improved insufficiently in mold shrinkage, those (Comparative Examples 4 and 9) have much lowered strength, and those (Comparative Examples 5 and 10) are unsatisfactory in mold releasability.

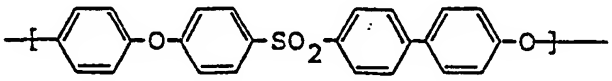
WHAT IS CLAIMED IS:

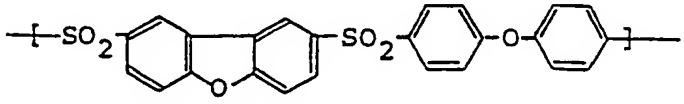
1. An aromatic polysulfone resin composition comprising 20 to 80% by weight of an aromatic polysulfone, 10 to 70% by weight of a fibrous reinforcement or an inorganic filler, and 0.5 to 20% by weight of a fluororesin, wherein the combined content of the fibrous reinforcement or inorganic filler with the fluororesin is 20 - 80% by weight based on the total weight of the composition.

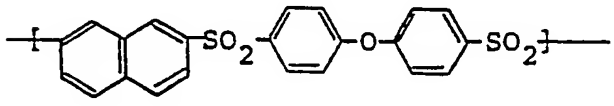
2. The resin composition of Claim 1, wherein the aromatic polysulfone is a polyarylene compound including arylene units, ether linkages and sulfone linkages, the arylene units, sulfone linkages and ether linkages being arranged in any sequence.

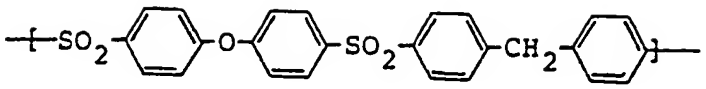
3. The resin composition of Claim 2, wherein the aromatic polysulfone includes the structure:

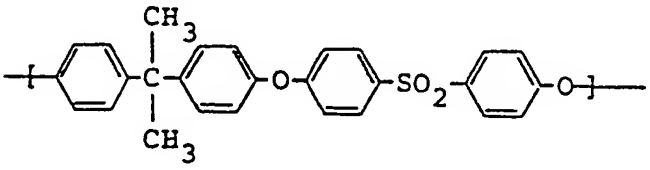
(1) 

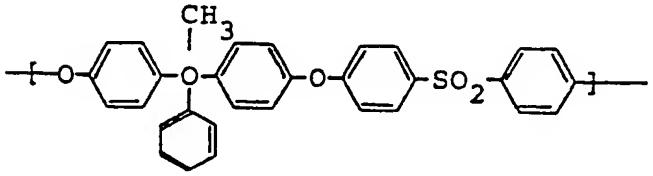
(2) 

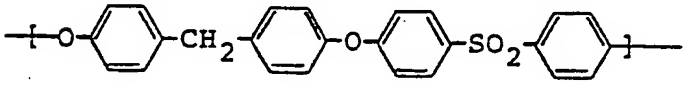
(3) 

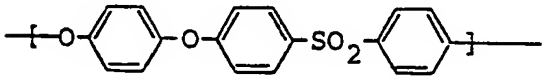
(4) 

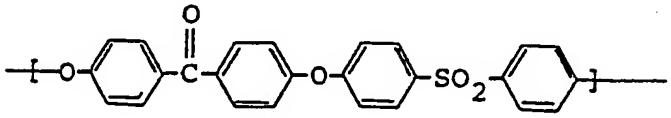
(5) 

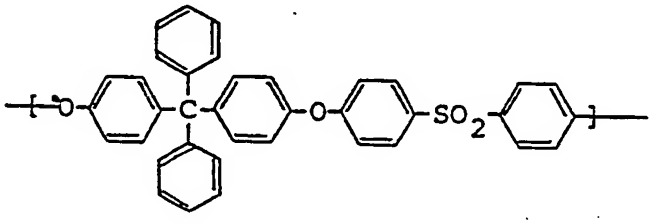
(6) 

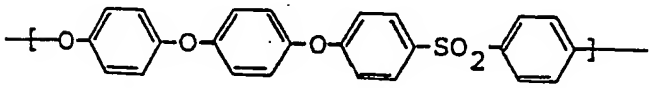
(7) 

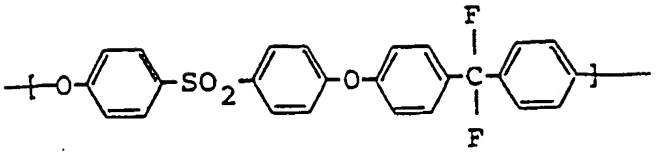
(8) 

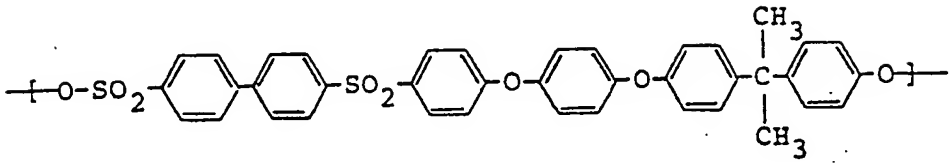
(9) 

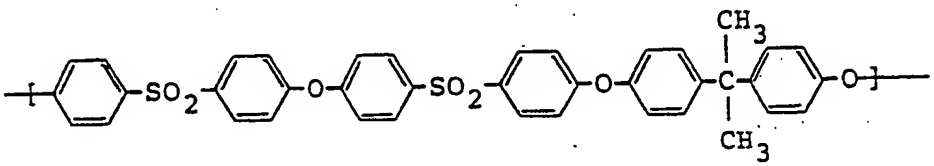
(10) 

(11) 

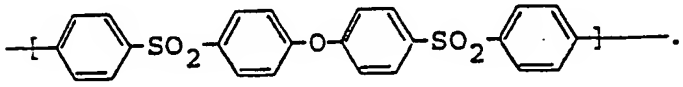
(12) 

(13) 

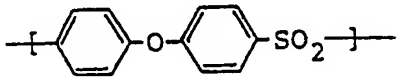
(14) 

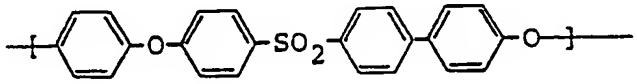
(15) 

or

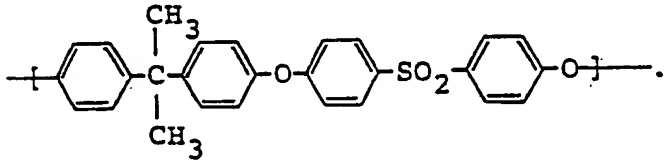
(16)  .

4. The resin composition of Claim 3, wherein the aromatic polysulfone has the structure:

(1) 

(2) 

or

(6)  .

5. The resin composition of any preceding Claim, wherein the reduced viscosity of the aromatic polysulfone is 0.3 to 0.6 as determined at 25°C on a 1 W/V % solution of the polymer in dimethylformamide.

6. The resin composition of any preceding Claim, wherein the fibrous reinforcement is at least one member selected from the group consisting of glass fiber, carbon fiber, aromatic polyamide fiber, silicon carbide fiber, silicon nitride fiber, alumina fiber, potassium titanate fiber and mineral fiber.

7. The resin composition of any preceding Claim, wherein the inorganic filler is at least one member selected from the group consisting of talc, calcium carbonate, magnesium carbonate, calcium sulfite, aluminum hydroxide, mica, molybdenum disulfide, wollastonite, graphite, titanium white, glass beads, zirconia, and silica.

8. The resin composition of any preceding Claim, wherein the fibrous reinforcement or the inorganic filler has been treated with a surface treating agent.

9. The resin composition of any preceding Claim, wherein the fluororesin is tetrafluoroethylene resin, tetrafluoroethylene-perchloroalkyl vinyl ether copolymer resin, tetrafluoroethylene-hexafluoropropylene copolymer resin, tetrafluoroethylene-ethylene copolymer resin, chlorotrifluoroethylene resin, or vinylidene fluoride resin.

10. The resin composition of Claim 9, wherein the fluororesin is tetrafluoroethylene resin.

European Patent Office

EUROPEAN SEARCH REPORT

0132094

Application number

EP 84 30 4646

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
X	FR-A-2 378 056 (ICI) * Claims 1,9,15; page 11, lines 7-34; page 12, lines 5-12; example 3 *	1-10	C 08 K 3/00 C 08 K 7/02 C 08 L 81/06 // (C 08 L 81/06 C 08 L 27/12)
A	CHEMICAL ABSTRACTS, vol. 99, no. 2, 11th July 1983, page 32, no. 6521m, Columbus, Ohio, USA; & JP - A - 58 05358 (HITACHI LTD.) 12-01-1983	6	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22-10-1984	HOFFMANN K.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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